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Corrosion Resistance in Sodium Chloride Solution of Ni-Co-P Electro-Brush Amorphous Coatings to replace hard chromium Coatings

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Abstract

To remanufacture damaged hard chromium plating devices, Ni-Co-P alloy brush coating is developed by electro brush plating technique. Surface morphology, element composition and phase structure are separately investigated by Scanning Electron Microscopy, Energy Spectrometer and X-ray Diffraction. The results show that Ni-Co-P alloy coating gets typical 'packet shape' morphology and amorphous phase structure, with 9.9wt% P element. The corrosion resistance of Ni-Co-P alloy coating is also studied by electrochemical experiments and immersion tests. The results show that its corrosion resistance is superior to that of hard chromium plating, can be applied to the remanufacture of damaged hard chromium plating equipment.

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***Keywords*:** Electro-brush plating; Amorphous coating; Phase structure; Corrosion resistance

1. Instruction

Remanufacture is series of technical measures and engineering activities to repair and reconstruct waste machinery and electronic products by means of advanced technology and industrial production, with the design and management of Entire Life Cycle (ELC) for machinery and electronic products as guidance, aiming at great-leap-forward promotion of waste machinery and electronic products, with guideline of high-quality, efficiency, energy saving, materials saving, environmental[1-3]. The chrome coatings have high corrosion resistance and wear resistance.

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It can greatly extend the service life of the mechanical parts, and has been widely applied in the mechanical remanufacture. However, the hexavalent chromium in waste water and waste gas causes serious pollution, several governments already adopted restrictive measures. Therefore, the study of new coatings, which are non-polluting and get high corrosion and wear resistance, to replace the chromium coatings, became a hot issue in the field of remanufacture [4-9].

Electro-brush plating technique enjoys the merits of potable equipment, technological flexibility, speedy plating, varied coating types, high bonding strength, wide adaptation, lower pollution and water and electricity saving. Therefore, it is a powerful tool for the mechanical remanufacture, especially for the on-the-spot repair of large machine parts without disassembly or partial urgent reparation [10-11]. The research follows the principle that, the co-deposition of Co and Ni can effectively reduce the stress of coatings and improve the coating structure and property, while the co-deposition of P element can form amorphous structure, which can improve the corrosion resistance of the coatings [12-15]. Ni-Co-P electro-brush amorphous coatings are developed. The corrosion resistance of Ni-Co-P coatings is evaluated by electrochemical experiments and immersion tests, also compared with hard chrome coatings.

2. Experimental Material and Methods

2.1. Coating preparation

The optimal composition of Ni-Co-P electro-brush amorphous alloy plating solution is determined after repeated experiments of formulation. The main components of the solution are as following: NiSO4•7H2O 250g/L, CoSO4•7H2O 25g/L, NaH2PO2•H2O 10g/L, NiCl2•6H2O 10g/L, HCl (36%) 30 ml/L, HCOOH 20ml/L, CH3COOH (37%) 70ml/L, and additive, maintaining pH at 0.5~1 and bath temperature at 20~50°C. The process is as following: wiping the coated workpiece for 2s without electricity, plating under voltage at 10~14V, maintaining the relative velocity between plating pen and workpiece at 10~20m/min, with analytical reagents and distilled water.

With 50mm×100mm×5mm 45 # steel as the substrate material, and DSD-75-S as electric power supply, the electro-brush plating process is as following: Sample polishing→ Electro cleaning (Forward, 10V, 60s)→ Activator 2 (Reverse, 10V, 60s)→ Activator 3 (Reverse, 12V, 30s)→ Plating working coatings→ Post-plating processing, cleaning with running water between each step.

Hard chrome coatings are prepared to make comparison with Ni-Co-P coatings. The preparation conditions of hard chromium sample are as following: CrO3 260g/L, H2SO4 2.6g/L, Temperature 52 ℃ , Current Density 25A•dm-2, Plating time 3h.

2.2. Structure and morphology

The surface morphology of electro-brush coatings is observed by Philips Quanta 200 scanning electron microscope (SEM) before and after the corrosion. The element composition of electro-brush coatings is determined by energy spectrometer on SEM. The phase structure is analyzed by Bruker AXS D8 X ray diffractometer. The microstructure is analyzed by JEM-2100 transmission electron microscope (TEM).

2.3. Evaluation of corrosion resistance

The corrosion resistance of hard chrome coatings, Ni-Co coating and Ni-Co-P coating are characterized by the electrochemical impedance spectroscopy (EIS) in 5 wt % NaCl solution. The EIS is measured by IM6e electrochemical workstation. The electrode system adopts the three-electrode system, with the coating as the working electrode, the saturated calomel electrode as reference electrode, and the nickel electrode as auxiliary electrode. The test conditions are as following: soaking the working electrode for 20min, with the AC signal amplitude of 5mV and the frequency response range at 10-1-105 Hz in the open circuit potential. Immersion experiment is used to value the corrosion resistance of these coatings. Three parallel specimens are immersed in 5% NaCl medium for 168h. The author get the specimens out every 24h, wash and dry them, weigh by analytical balance accurately up to 10-4 gram, get the mean value as the weightlessness of samples, and observe the surface morphology of the coatings after corrosion.

3. Results and discussion

3.1. Surface morphology and structure

Figure 1 shows the surface morphology of Ni-Co-P coating. It can be seen that, the Ni-Co-P coating presents the typical ‘potato-like’ morphology. This is due to the adding of sodium hypophosphite changes the deposition process of the coating elements, forming concentration ups and downs at the coating deposition interface, which leading to the uneven coating surface. Table 1 shows the element content of Ni-Co Coating and Ni-Co-P Coating. The element content of Ni-Co-P alloy coating is as following: P 9.90wt%, Ni 50.54 wt%, and Co 24.40wt%.

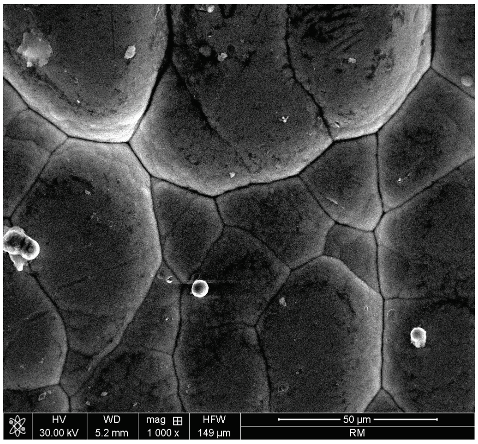

Fig. 1. SEM images of Ni-Co-P coating.

Table 1. Element ratio of electro-brush plating Ni-Co and Ni-Co-P.

Electro-brush plating	Ni (*wt%*)	Co(*wt%*)	P(*wt%*)
Ni-Co	39.23	44.33	—
Ni-Co-P	50.54	24.40	9.90

Figure 2 shows the XRD patterns of Ni-Co-P alloy plating. It can be seen that, the corresponding characteristic peak of Ni-Co-P coating is broadened, performing as the spectrum characteristics of amorphous coating, which indicates that, under the influence of the P element, the structure of the most part of coating changes into the amorphous structure. The calculating finds that, the amorphous degree of Ni-Co-P alloy plating reaches 67%.

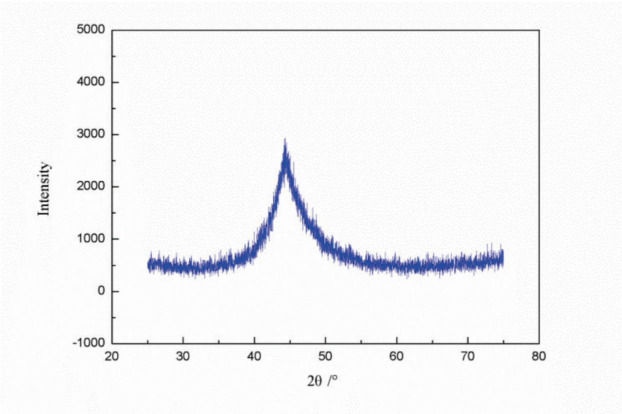

Fig. 2. XRD spectra of Ni-Co-P coating.

Figure 3 shows the bright field image and electron diffraction image of Ni-Co-P coating. As can be seen, the bright field of Ni-Co-P coating is uniform and transparent, the electron diffraction pattern is a diffuse halo spot, which is the typical diffraction pattern of amorphous phase, indicating that the electro-brush coating contains obvious amorphous structure.

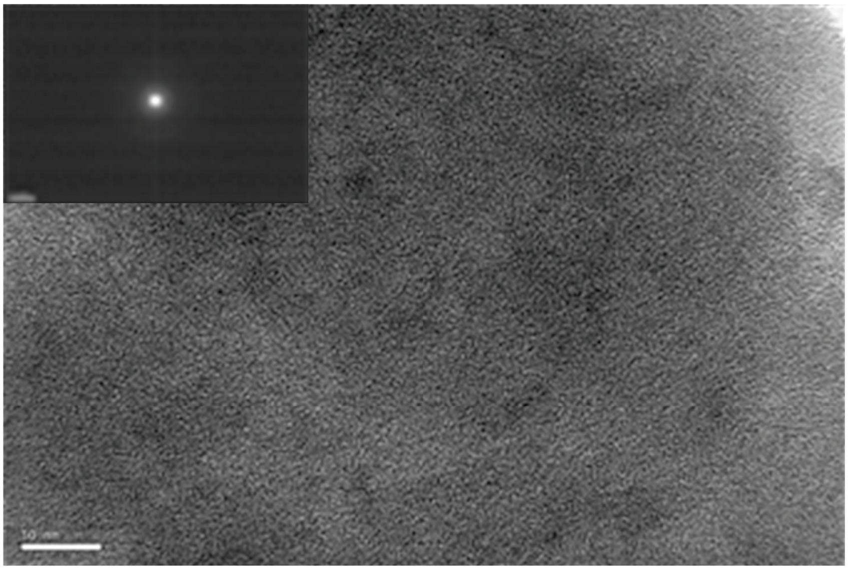

Fig. 3. Bright field image and diffraction pattern of Ni-Co-P coating.

3.2. Electro-chemical corrosion resistance of the coating

AC impedance spectra of Ni-Co-P amorphous coating and chrome coating measured in 5% NaCl solution is shown in Figure 4, the test results of the impedance are demonstrated by the complex plane (Nyquist diagram).

As can be seen from Figure 4, the capacitive reactance of Ni-Co coating is smaller than chrome coating, while Ni-Co-P coating is greater than chrome coating, therefore, the corrosion resistance of Ni-Co-P amorphous coating is better than chrome coating.

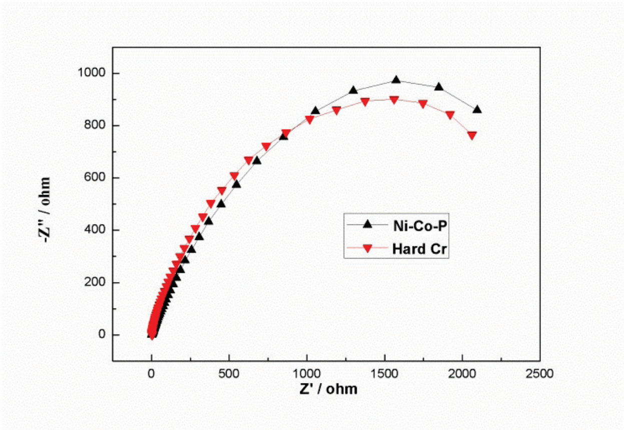

Fig. 4. EIS plots of hard chrome and Ni-Co-P coatings in 5%NaCl.

The equivalent circuit using EIS impedance spectroscopy obtained from Nyquist plot is shown in Figure 5. R2 represents the charge transfer resistance, indicating the corrosion resistance of coating. The fitting results find that the transfer resistance of the Ni-Co-P amorphous coating is 3240Ω/cm^2, exceeding chrome coating of 2229Ω/cm2, which means that the corrosion resistance of Ni-Co-P amorphous coating is significantly better than chrome coating. It is due to the amorphous organization in Ni-Co-P coating can effectively improve the corrosion resistance.

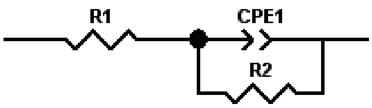

Fig. 5. Equivalent circuit of EIS plot.

3.3. Immersion corrosion resistance

The samples are kept in 5% NaCl solution (25℃) at room temperature for 168h, measured the weight daily, and calculated the total weight loss. The weight loss results are shown in Figure 6.

As can be seen from Figure 6 that, the total corrosion weight loss of Ni-Co-P coating is 6.6 mg/cm^2 for168h, significantly lower than the corrosion weight loss of hard chrome coating of 14.3mg/cm^2, approximately reducing 53.8%. It shows that the corrosion of Ni-Co-P coating is significantly better than hard Cr coating. From the beginning to 96h, the corrosion weight loss of Ni-Co-P coating and hard chrome coating is roughly equal, and these two coatings present good corrosion resistance. After 96h, the corrosion weight loss of hard chrome coating significantly accelerates, while the weight loss of Ni-Co-P coating is still very slow, and the corrosion resistance of amorphous brush Plating. The analysis indicates that, after 96h immersion, the non-uniform part of the hard chrome coating corrodes to the substrate, and some of the coating begins to fall off.

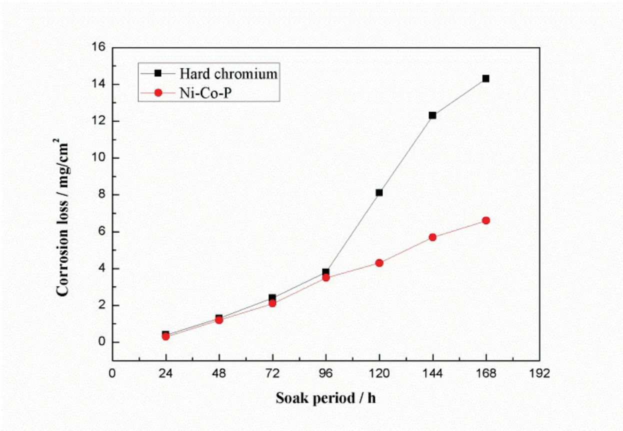

Fig. 6. Corrosion weight loss of hard chrome and Ni-Co-P coatings in 5% NaCl.

3.4. Surface morphology after corrosion

Figure 7 shows the surface morphology of hard chrome coatings after 7 days corrosion in 5% NaCl solution. It can be seen from Figure 7, the surface of hard chrome plating is uneven after corrosion, with sloughing of large areas of the chrome coating along the crack, and more serious corrosion of the substrate. It is due to the large number of micro-cracks on the surface of hard chrome coating. Under the corrosion of Cl-, the base metal and hard chrome coating constitute the primary cells of corrosion. The Coating is cathode coating, which accelerates the corrosion of the substrate. During the corrosion process, the substrate corrosion exacerbated, and the chrome coating also shed. It can be seen from the enlargement of local chrome coating after corrosion, there are a lot of pores with different size on the surface of hard chrome coating. This is due to that, in NaCl solution, Cl- adsorbs in the surface of the chrome coating, destructs the passivation film of the hard chrome coating, leading to serious pitting.

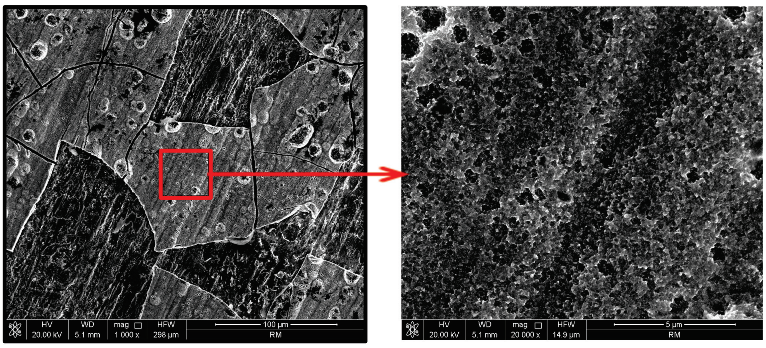

Fig. 7. SEM of hard chrome coating after corrosion for 7 days in 5% NaCl.

Figure 8 shows the surface morphology of Ni-Co-P coating after 7 days corrosion in 5% NaCl solution. It can be seen from the figure that, Ni-Co-P coating maintains good integrity and uniform surface after the immersion corrosion, without coating sloughing along the crack. There are less flocculent corrosion products at the junction of ‘potato-like’ morphology, which leading to better corrosion resistance. Evaluating the corrosion resistance with the corrosion weight loss as the index, the corrosion resistance of Ni-Co-P coating is increased by about 100% than hard chrome coating, superior to hard chrome plating.

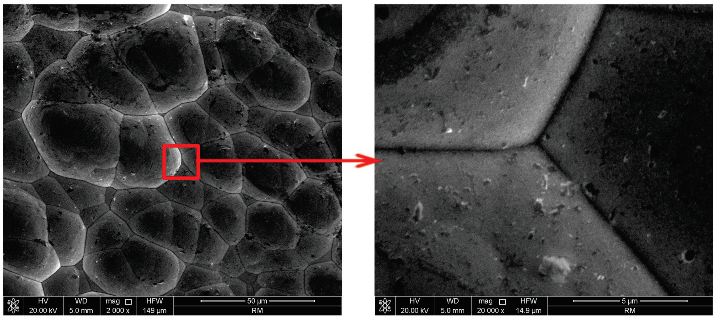

Fig. 8. SEM of Ni-Co-P coating after corrosion for 7 days in 5% NaCl.

4. Conclusions

- Ni-Co-P electro-brush amorphous alloy coating is prepared by electro-brush plating technique with smooth surface, compact structure, and ‘potato-like’ morphology. The content of P reaches 9.9%, while the amorphous rate of the coating arrives at 67%.

- The electro-chemical experiments and immersion tests show that the corrosion resistance of Ni-Co-P coating is better than hard chrome coating.

- The good corrosion resistance of Ni-Co-P amorphous brush coating is due to its dense layer organization and amorphous structure, the reason for the poor corrosion resistance of the hard chrome coating is the large number of cracks on the surface, leading to the coating easily falling during the corrosion.

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